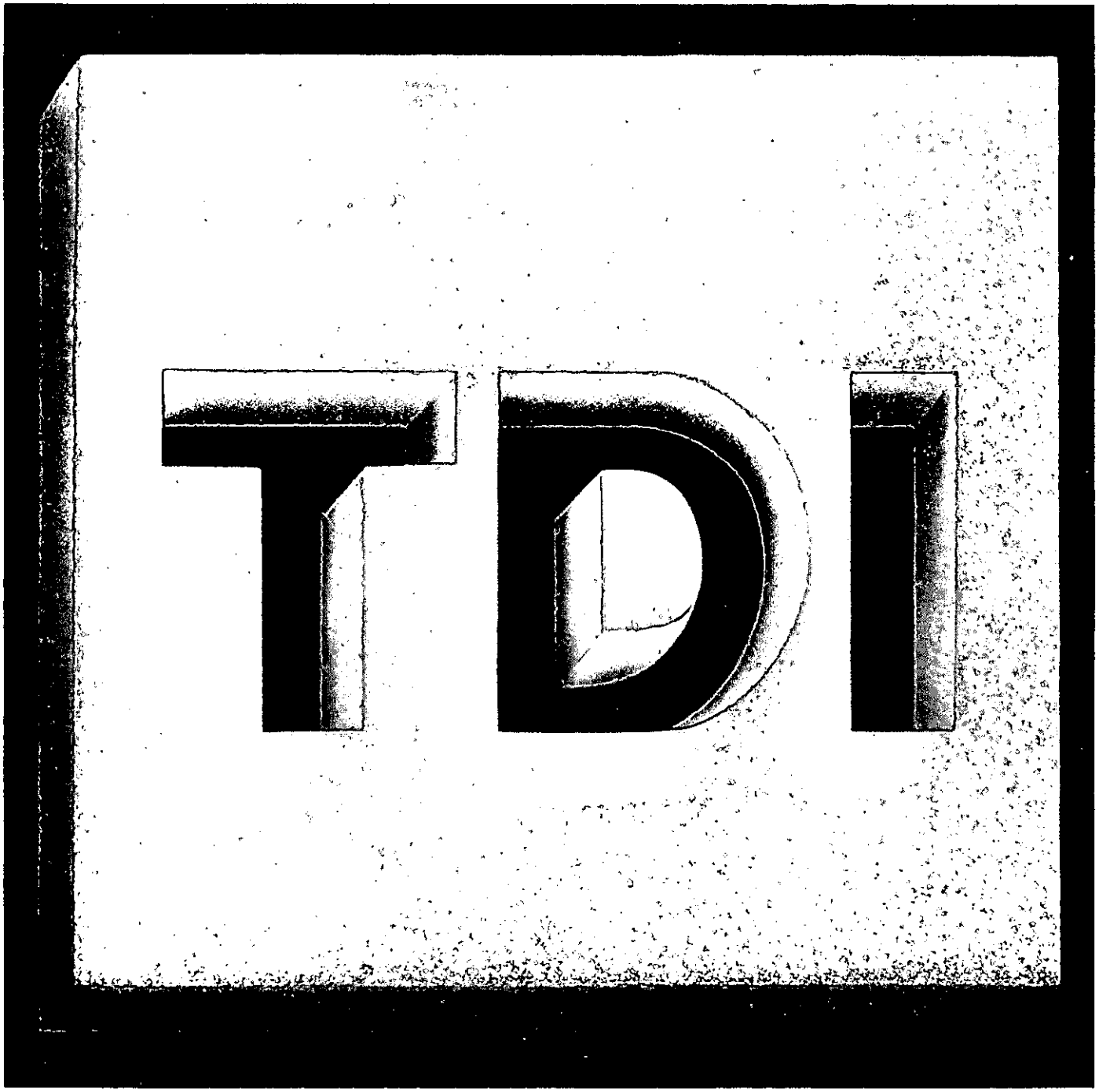
TOLUENE DIISOCYANATE



Olin CHEMICALS

INTRODUCTION

Olin toluene diisocyanate (TDI) is produced at Lake Charles, La., and Moundsville, W. Va. The two have a combined annual capacity approaching 200 million pounds — making Olin the second largest producer of TDI in the world.

Our position as a TDI supplier is particularly strong because Olin is one of the few manufacturers independent of outside sources for such key precursor chemicals as chlorine, ammonia and nitric acid. In fact, Olin's degree of integration for producing TDI is unmatched by any other U.S. supplier.

Independence in raw materials and the security of two producing plants make Olin a particularly reliable TDI source for the urethanes industry.

Olin in Urethanes

Olin's experience in urethanes goes back more than 20 years. In addition to TDI, Olin produces many other products for rigid and flexible foams and for non-foams. These products include: polyether polyols, rigid foam systems (chemicals and dispensing equipment) and flame retardants*.

Olin urethane products are produced in five plants in the U.S. and in three more overseas. Domestically, all products are available at the plants and various products are available from urethane distribution centers in New Jersey, Indiana, Texas and California. (For availability of TDI, see page 3.)

Olin can provide valuable on-site assistance, including a seminar on safety and handling, to users of TDI and other urethane products. Additional comprehensive analytical capability and technical services are available from our Application Research and Customer Service Laboratories in New Haven, Connecticut.

If you have any questions regarding the application, handling or use of TDI not answered by this brochure, please contact your nearest Olin Sales Office (see back cover). Or write: Market Manager, TDI, Olin Chemicals, 120 Long Ridge Road, Stamford, CT 06904.

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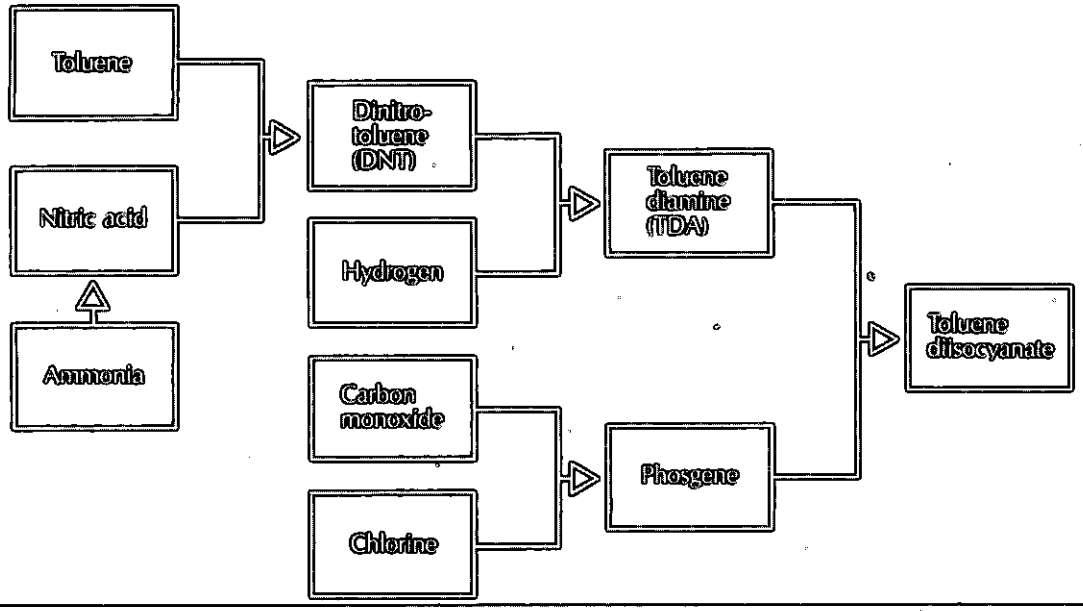
Figure 1. Steps in the Production of Toluene Diisocyanate

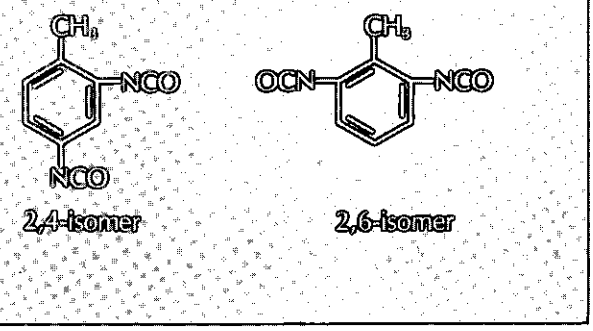


*The term "flame retardant" is a relative term and is not intended to indicate hazards presented by foams under actual fire conditions.

PROPERTIES

Olin toluene diisocyanate is referred to as TDI-80 because it is an 80:20 mixture of the 2,4- and 2,6-isomers of TDI. Structural formulas of these isomers are shown in Figure 2.

Figure 2. Structural Formulas of TDI Isomers



Olin produces TDI-80 in two forms, designated Type I and Type II. Both have the 80:20 isomer ratio, but they differ slightly in acidity and hydrolyzable chloride content.

Type I is used in foam and non-foam urethanes. Type II is used in non-foam urethanes, rebonded flexible foam, and other applications.

Physical properties of TDI-80, Types I and II, are shown in Figure 3. Those properties marked by an asterisk (*) are Olin specifications; others are typical of commercially available TDI.

TDI has a sharp, pungent, sweetish odor. Its vapors are toxic. For this reason, certain precautions are necessary when handling or using toluene diisocyanate. For complete information, see "Handling TDI," page 10.

Reactivity

Olin TDI is a clear liquid, water white to light yellow in color. It yellows on exposure to light.

Chemical. TDI is a base. It reacts readily with compounds containing active hydrogens, such as acids and alcohols. Contact with other bases, such as caustic soda or tertiary amines, might cause uncontrollable polymerization and the rapid evolution of heat.

Water. On contact with water, aromatic poly-substituted ureas ("polyurea") are formed, and carbon dioxide plus heat are evolved. In time, white urea crystals will precipitate.

Heat. High temperatures can cause formation of dimer and discoloration of the TDI. This phenomenon is time-and-temperature related (see Figure 4). When the level of dimer approaches 1% by weight, solid dimer forms as needle-like white crystals. These crystals cannot be completely filtered out because the solution is supersaturated and new crystals are formed.

Low temperatures, below 15°C (59°F), cause TDI to freeze. Frozen TDI is also white and crystalline.

NOTE: As can be seen from the above discussion, if white crystals are detected in TDI they may be frozen TDI, polyurea or dimer. For suggestions in dealing with this situation, see "What To Do In Case Of . . .", page 10.

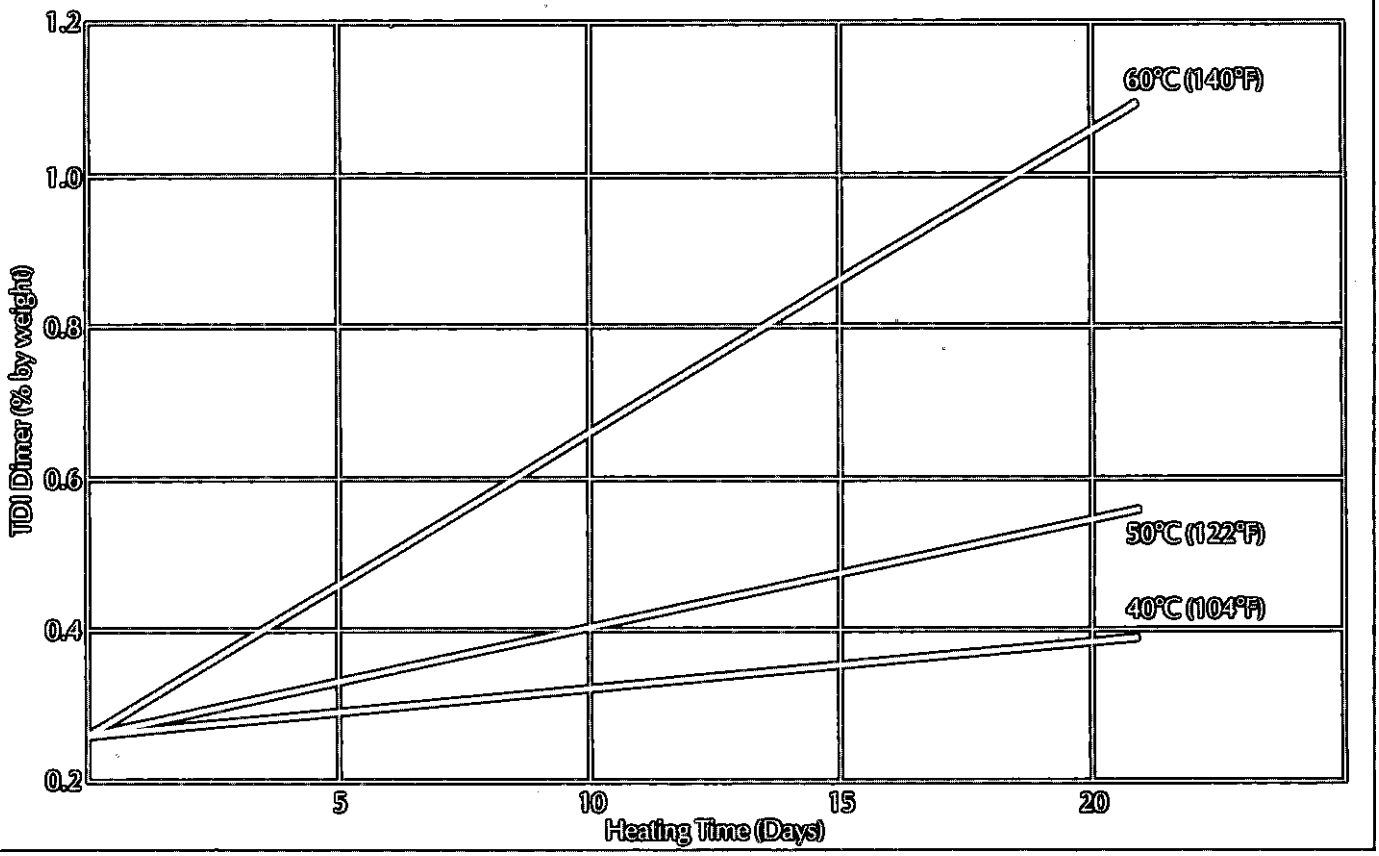
Figure 3. Physical Properties

Molecular Weight	174.163
Assay*, min (%)	99.7
Isomer Ratio* (%)	
2,4-isomer	80 ± 1
2,6-isomer	20 ± 1
Acidity*, as HCl (%)	
Type I	0.002-0.004
Type II	0.008-0.010
Hydrolyzable Chlorides * (%)	
Type I	0.003-0.008
Type II	0.011-0.014
Chlorine*, max (%)	0.20
Ash (ppm)	20
Color (APHA)	15
Specific Gravity @ 25/25°C [77/77°F]	1.22 ± 0.01
Density (lbs per gal)	
@ 15.5°C [60°F]	10.23
@ 20°C [68°F]	10.14
@ 38°C [100°F]	10.02
@ 60°C [140°F]	9.86
Viscosity (cs)	
@ 50°C [122°F]	1.5
@ 100°C [212°F]	0.8
@ 135°C [275°F]	0.5
Melting Point Range (°C)	11.5-13.5
(°F)	52.7-56.3
Freezing Point	
2,4-isomer (°C)	15.0
(°F)	59.0
2,6-isomer (°C)	7.2
(°F)	45.0
Boiling Point	
@ 10mm Hg (°C)	121
(°F)	250
@ 760mm Hg (°C)	251†
(°F)	484†
Flash Point‡, COC (°C)	135
(°F)	275
Fire Point, COC (°C)	142
(°F)	288
Latent Heat of Evaporation (Btu/lb)	
@ 120°C [248°F]	131
@ 180°C [356°F]	121
Vapor Density, air = 1	6
Vapor Pressure, approx. (mm Hg)	
@ 20°C [68°F]	0.01
@ 120°C [248°F]	10
@ 130°C [266°F]	16

* Olin Specification
† Decomposes

‡The flammability properties of this material (or any other material) are not intended to reflect the fire hazards presented by any resultant cellular or foamed plastic product.

Figure 4. TDI Dimer Formation Over Time at Various Temperatures



TDI SHIPMENTS

Olin TDI-80 is produced in Lake Charles, Louisiana, and Moundsville, West Virginia. It may be obtained from these plants in tank cars, tank trucks or drums. Olin TDI is also shipped to distribution centers in Texas and California. TDI can also be exported, via ocean vessels, from these distribution centers.

Regardless of type of shipping container, TDI is always shipped under a nitrogen pad to prevent contamination by water vapor. To estimate weight of the contents of a given container, multiply the number of gallons by 10 (e.g. a 55-gallon drum contains 550 lbs of TDI).

Tank cars. TDI is usually shipped in cars of 20,000-gallon capacity. Other sizes, however, are also available. Although all cars have exterior coils and are insulated, Olin cannot guarantee arrival temperatures with tank car deliveries.

Tank trucks. Capacity is 4,000 gallons. Tanks are constructed of lined steel or stainless steel. Though not all trucks are insulated, Olin delivers at temperatures within the range specified by the customer.

Drums. TDI-80 is available in 55-gallon non-returnable drums constructed of a minimum of 18-gauge steel, with a phosphatized interior.

Ocean vessels. Olin has the capability to serve world markets with shipments of large quantities of TDI in ocean tankers. Evaluation of this possibility involves the coordinated advice of marine transportation, technical service and production personnel.

UNLOADING

Customers should give careful consideration to the way that TDI will be received. Adequate facilities must be provided (see "Storage of TDI," page 9).

Toluene diisocyanate is regulated by the Department of Transportation (DOT) as a Class B poison. Since TDI can cause serious injury to the lungs, eyes and skin, all workers must wear protective clothing and equipment. They should observe all prescribed safe-handling procedures and practices. The section of this brochure entitled "Handling TDI" should be carefully read by, and explained to, all employees.

Temperature

TDI-80 is normally loaded into insulated tank cars or trucks at 24-30°C (75-86°F); in winter, at 38-43°C (100-110°F). On arrival, the temperature of the TDI should be taken. Recommended unloading temperature is 21-30°C (70-86°F).

If the temperature is between 17°C and 21°C (62-70°F) the TDI can be heated. If the temperature is below 17°C it is likely that there is some freezing, and the TDI must be thawed.

For methods of temperature measurement and thawing TDI in tank cars, see page 7.

Sampling

A sample of TDI should be taken for testing before unloading a tank car, truck or drum. While this is being done, goggles and other necessary protective equipment must be worn (see page 11).

Olin tank trucks are equipped with a sampling tube. For tank cars, the preferred procedure is to take the sample from the unloading line (through a customer-installed valve). This avoids opening the manway cover and loss of the nitrogen pad, and thus eliminates a possible source of contamination.

If a sample is taken through this valve, first flush out 1-5 gallons of TDI (for proper disposal procedure, see "Handling Spills & Leaks," page 12). Flushing ensures that a representative sample is being taken. This is particularly important in determining if urea or dimer (white precipitates) are present.

If a sample must be taken directly from a pressurized car or truck manway, be sure it is an "all-level" sample, taken from each compartment, at or near atmospheric pressure. Car hatches should be open for as little time as possible. During inclement weather make provision to prevent contamination of the product.

Procedure for an All-Level Sample

The sample is taken using a glass bottle in a weighted bottle holder. To be sure of getting a representative sample, the bottle holder should be lowered to the bottom and then withdrawn at such a rate that the bottle is not quite full when it reaches the surface. (This may take some practice.)

The bottle should then be capped, cleaned and plainly labeled with product lot numbers, tank car or truck number, compartment number (if more than one), date and sampler's initials.

NOTE: While the following section is on unloading tank cars, many of the principles apply to receipt by other means, and employees should be familiar with them.

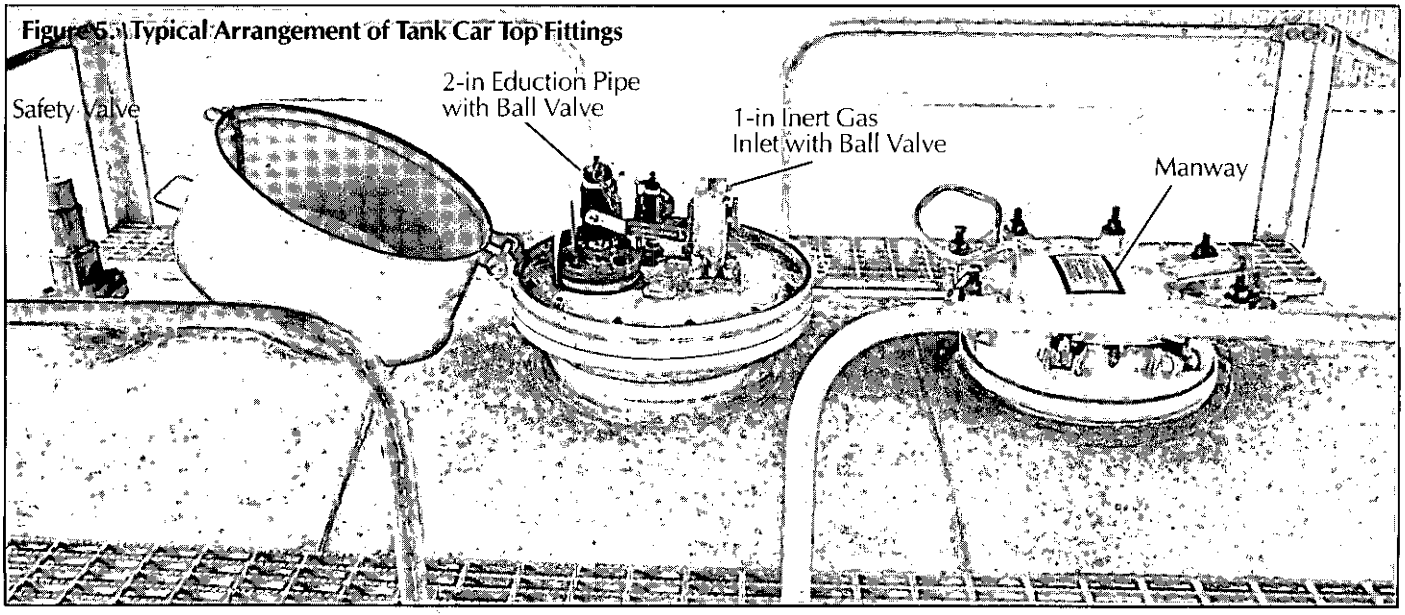
TDI Tank Cars

Olin operates a large fleet of dedicated TDI tank cars. Most have a capacity of 20,000 gallons, although other sizes are available. Figure 5 shows a typical arrangement of the top fittings. While there may be some differences in the location of the fittings on the top of the car, the following are on every TDI car, regardless of type:

Manway
Safety valve
2-inch eduction pipe with a ball valve
1-inch inert gas inlet valve

All of the cars are designed for top unloading through the eduction pipe (Figure 6). Some cars originally could be unloaded from the bottom. (Some of these have internal foot valves which can be identified by a valve handle on the top of the car.) However, on most of the cars which could be bottom unloaded the valves have been permanently closed. Even on those where bottom unloading is still possible, top unloading is the preferred method.

Figure 5. Typical Arrangement of Tank Car Top Fittings



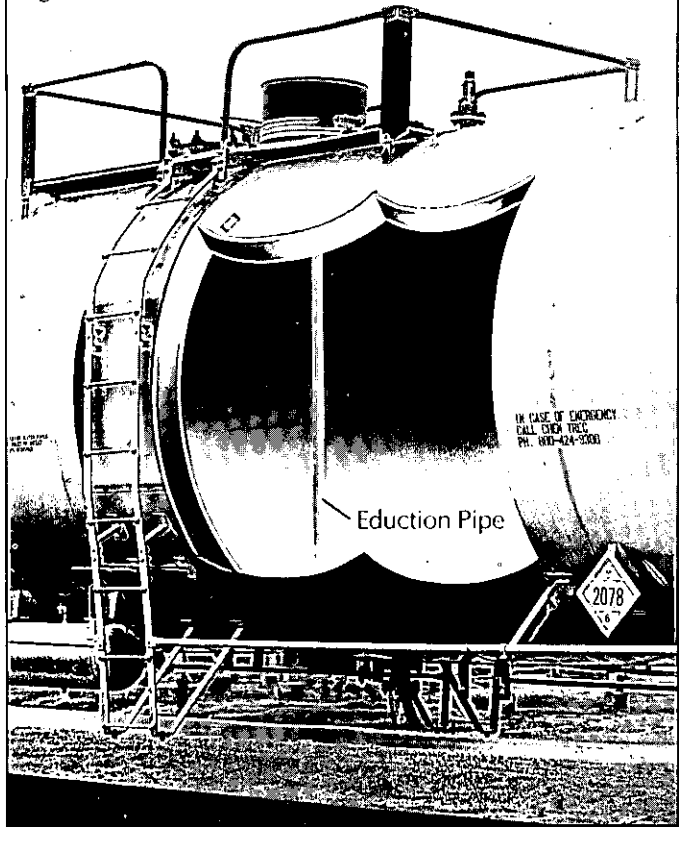
TDI tank cars are insulated to prevent freezing. However, in the event freezing occurs, all cars have steam coils for thawing the TDI and the bottom outlet valves (see "Thawing TDI Tank Cars," page 7).

Tank Car Unloading — General

Department of Transportation regulations for unloading tank cars are given in Section 174.67 of Title 49 Code of Federal Regulations, *Hazardous Materials Regulations*. All persons responsible for tank car unloading should be familiar with these regulations and all applicable requirements should be observed. Some of those requirements are:

1. Unloading operations must be performed only by reliable persons properly instructed in unloading hazardous materials and made responsible for careful compliance with this part. [174.67 (a) (1)]
2. Brakes must be set and wheels blocked on all cars being unloaded. [174.67 (a) (2)]
3. Caution signs must be so placed on the track or cars to give necessary warning to persons approaching the cars from the open end of a siding. Signs must be left up until after the cars are unloaded and disconnected from the discharge connection. [174.67 (a) (3)]
4. Unloading connections must be securely attached to unloading pipes on the dome or to the bottom discharge outlets before any discharge valves are opened. [174.67 (h)]
5. Tank cars may not be allowed to stand with unloading connections attached after unloading is completed. Throughout the entire period of unloading, and while car is connected to unloading device, the car must be attended by the unloader. [174.67 (i)]

Figure 6. Sectional View of Tank Car



6. If necessary to discontinue unloading a tank car for any reason, all unloading connections must be disconnected. All valves must first be tightly closed, and the closures of all other openings securely applied. [174.67 (j)]
7. As soon as a tank car is completely unloaded, all valves must be made tight, the unloading connections must be removed and all other closures made tight, except that heater coil inlet and outlet pipes must be left open for drainage. If it has been opened, the manway cover must be reapplied by the use of a bar or wrench, the outlet valve reducer and outlet valve cap replaced by the use of a wrench having a handle at least 36 inches long, and the outlet valve cap plug, end plug, and all other closures of openings and of their protective housings must be closed by the use of a suitable tool. [174.67 (k)]

Other important suggestions which are not part of the regulations are:

1. The tank car must be protected during unloading by such means as derails or locked switches.
2. The contents of the car tank should only be unloaded during daylight hours or when adequate lighting is provided.
3. Ample water should be available at the unloading site. This should include a shower equipped with a quick-opening, deluge head, and an eyewash fountain.
4. If the unloading area has heavy traffic it should be roped off and passersby warned by posting of "Danger—TDI" signs.

Top Unloading of TDI

This is the only method possible for most cars, and the preferred method for all cars. Figure 7 shows how unloading is accomplished by using an inert gas such as nitrogen or dry air (−40°C dew point). This dry atmosphere padding is necessary in order to prevent a reaction between the TDI and any water vapor which might be present. Under no circumstances should a combustible gas be used; it presents an explosion hazard.

All fittings should be inspected for evidence of potential leaks before the tank and piping system are pressurized. An oil trap should be installed on the inert gas supply line.

Tank cars are protected by a safety valve. The pressuring system should be designed so as not to exceed a safe working pressure. Thirty psig is suggested as a maximum, regardless of the capacity of the tank car. Lower pressures are desirable and 10-20 psig is recommended.

The preliminary steps of positioning the car and installing the necessary safety devices must be carried out in accordance with the instructions outlined in the *Tank Car Unloading* sub-section, above.

Before unloading, check the temperature of the TDI and take a sample. Then:

1. Secure the tank car manway if it has been opened. Make sure the storage tank is adequately vented.
2. Remove the 1-inch plug from the inlet valve and connect the inert gas line (see Figures 5 and 8).
3. Check the unloading line for proper temperature of 21-30°C (70-86°F). Preheat the line if necessary, and connect it to the eduction pipe.

4. Open all valves in the unloading line.
5. Open the inert gas supply valve. The pressure on the car will effectively be established by the setting of the inert gas valve. The flow of TDI can be controlled by a valve in the unloading line.

After unloading is complete:

1. Clear the unloading line and equalize the line pressure. Disconnect the unloading line and cap it.
2. Disconnect the steam lines and blow out the coil with inert gas. Do not replace the caps on the steam line.
3. Repressurize the car to 10 psig with nitrogen.
4. Secure the dome housing.
5. Reverse all four placards and return the car by prescribed routing.

Bottom Unloading of TDI

Olin strongly advises against bottom unloading TDI and, in fact, bottom unloading is impossible on most Olin cars. However, if cars must be bottom unloaded, contact Olin Technical Service for suggested procedures.

Cars which can be unloaded from the bottom come in two types: those with a 4-inch exterior ball valve, and those which have an internal foot valve. Most cars also have a 2-inch reducer auxiliary ball valve.

Cars with an internal foot valve can be identified by the combination valve handle/cover on the top of the car. In order to open the valve the cone-shaped cover must be removed, inverted and reattached. To open, rotate counterclockwise.

When finished, close the valve, invert the cover and replace in its original position. This cover cannot be replaced unless the valve has first been closed.

Unloading Tank Trucks

Tank trucks are unloaded by the driver of the vehicle. He is responsible for following proper safety rules. However, it is the recipient's responsibility to provide competent supervision and safety equipment. The supervisor should make sure the unloading area is clear and adequate facilities are ready for receiving the shipment. The unloading area should be level and paved so the truck can be easily maneuvered to the proper spot.

On tank trucks used for short hauls insulation is not necessary. However, insulated trucks are often used to maintain proper temperature, particularly for longer hauls or colder weather.

The arrival temperature of the TDI must be above 21°C (70°F). If the temperature is below 21°C it is the trucking company's responsibility to correct it.

After the temperature has been checked (and adjusted, if necessary) a sample of the shipment should be taken. Tank trucks are equipped with a sampling tube for this purpose.

Unloading Drums

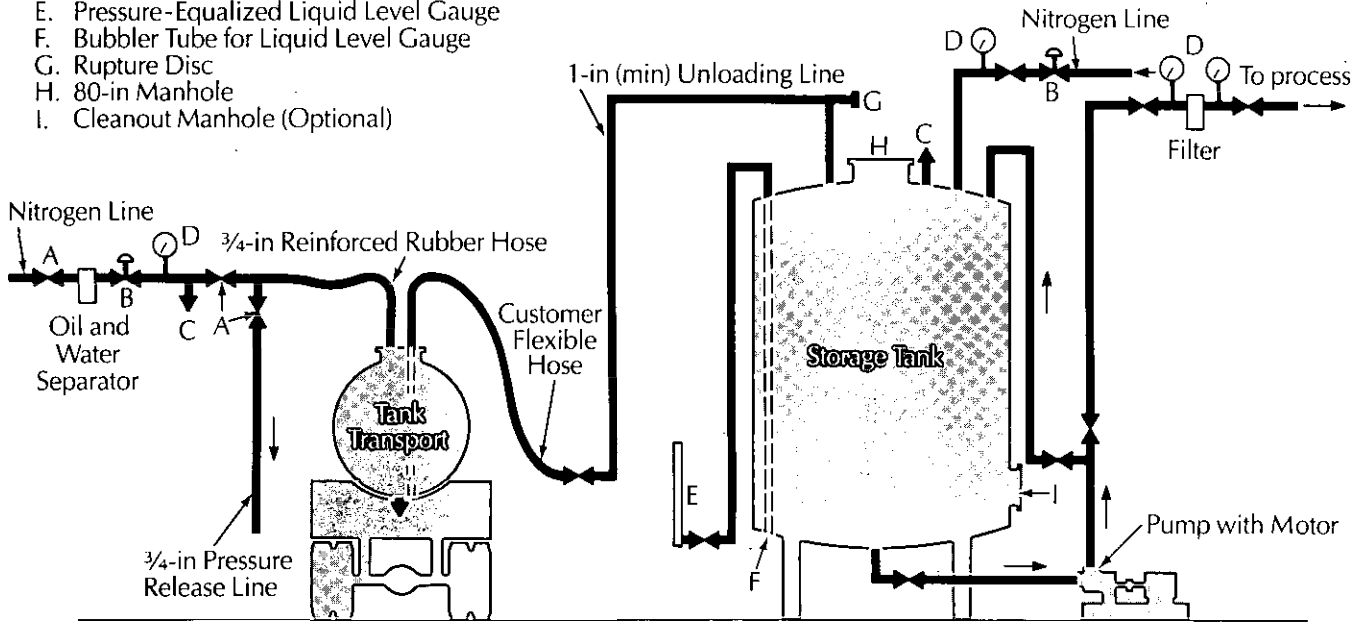
Follow all applicable safety procedures. Be sure full protective clothing is worn when opening the drum plug (bung), when placing or operating pumps, or when flushing out empty drums. In the event of spillage, see page 12.

If the TDI is frozen, or if there is a possibility of freezing

Figure 7. Top Unloading and Storage Arrangement

A. Globe Valve
B. Pressure Regulating Valve
C. Pressure Relief Valve
D. Pressure Gauge
E. Pressure-Equalized Liquid Level Gauge
F. Bubbler Tube for Liquid Level Gauge
G. Rupture Disc
H. 80-in Manhole
I. Cleanout Manhole (Optional)

Note: Tank transport to be equalized with storage tank with 1-in (min) line as shown or maintained with 10 psig nitrogen.



because drums have been exposed to ambient temperatures below 17°C (62° F), then the drum should be heated to 35-40°C (95-105° F) until all TDI is liquid. Heating above 40°C should be avoided. After being thawed, the drums should be rolled for at least 30 minutes to uniformly mix the 2,4- and 2,6-isomers.

Drums should be kept under a nitrogen or dry air (−40°C dew point) pad to prevent contamination by water vapor. However, unloading by pressure is unsafe. The preferred method is by pump, manual or electric (see Figure 9). If the pump is electrical be sure the drum is properly grounded. If drums are to be emptied by gravity the faucets should be self-closing. Bungholes should be fitted with a dryer-breather vent device to prevent drum collapse.

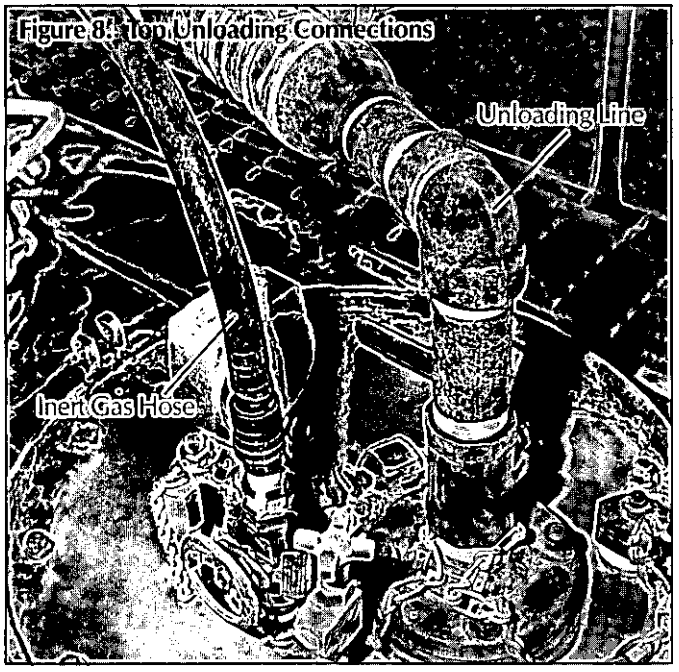
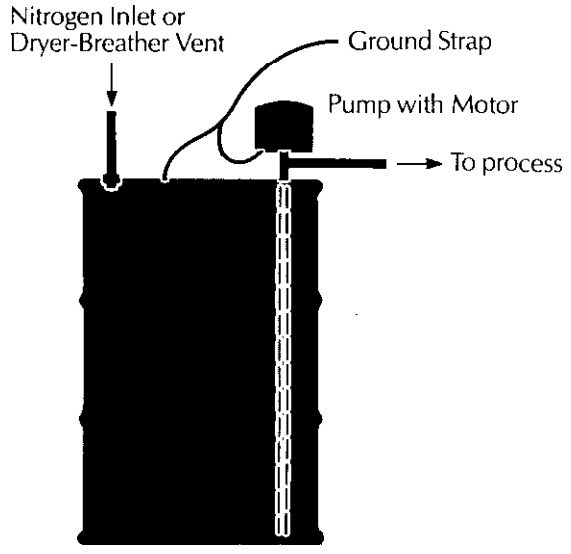


Figure 8. Top Unloading Connections

Figure 9. Drum Unloading System



THAWING TDI TANK CARS

TDI is shipped in insulated tank cars. During the winter it is loaded at temperatures between 38 and 43°C (100-110° F). Despite these precautions there may be substantial heat loss before the car reaches its final destination.

Therefore, during the winter all incoming tank cars of TDI should be checked for freezing.

The 2,4-isomer of TDI-80 freezes at 15°C (59°F); the 2-6-isomer at 7.2°C (45°F). Between these two temperatures only the 2,4-isomer freezes. If this happens isomer stratification takes place. However, if proper care is taken in thawing TDI, the quality can be maintained and no foaming problems should occur.

How to Determine if TDI is Frozen

There are two ways to tell if freezing has taken place: (1) visual inspection of the car's contents and (2) measuring TDI temperature. Temperature measurement is the preferred method because it is more accurate and will detect frozen TDI even when it is not visible.

Temperature measurement. Some tank cars contain a stainless steel thermowell under the dome cover. Simply insert a thermocouple into the thermowell and read the temperature.

If the temperature is less than 17°C (62°F) it is likely that the car contains some frozen TDI.

With cars which do not contain a thermowell, a thermometer must be inserted into the tank car. *A self-contained breathing apparatus should be worn as protection from TDI fumes.*

Release the pressure from the car by opening the one-inch pressure release valve. A thermometer can then be inserted through this ball valve. Or, the dome can be opened and the thermometer inserted through the dome. The thermometer should be lowered to the bottom of the car, then slowly removed.

When taking the temperature, use a Min/Max[a] thermometer. A conventional thermometer may give an erroneous reading because the ambient temperature is usually lower than the internal TDI temperature.

Visual inspection. Release the pressure on the car by opening the one-inch air release valve, then open the dome. *A self-contained breathing apparatus should be worn as protection from TDI fumes.*

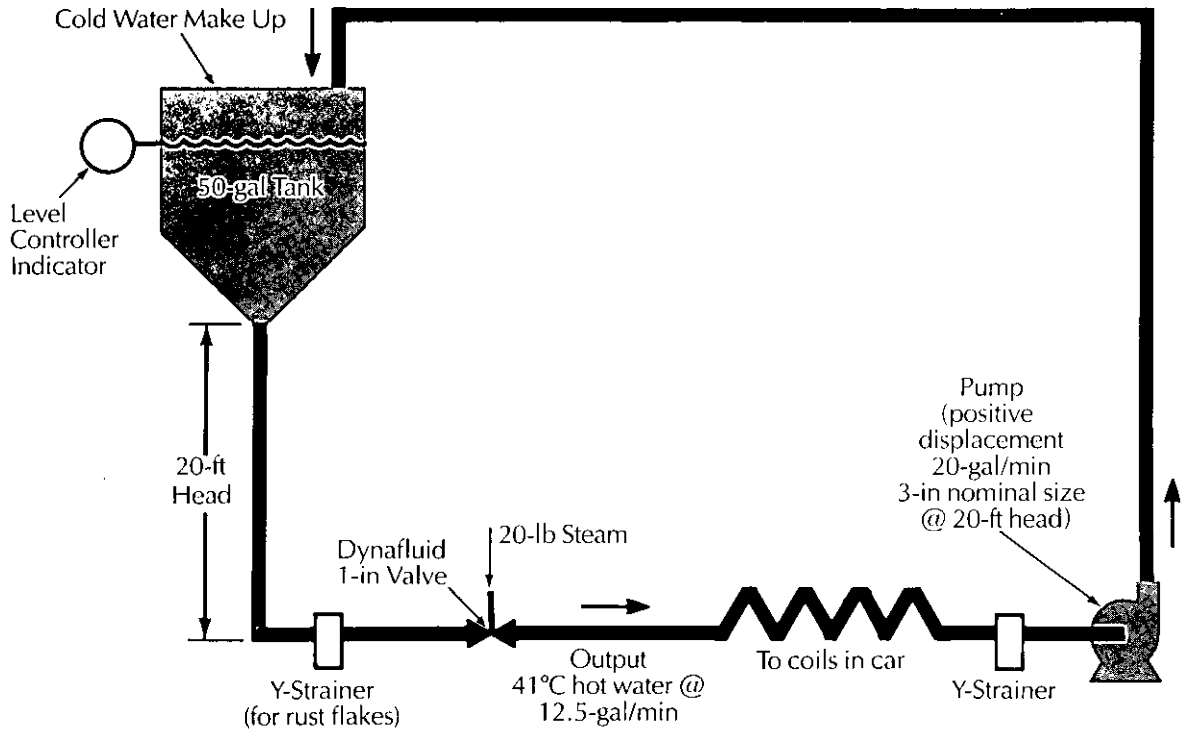
By looking inside the tank car it is frequently possible to detect the presence of frozen TDI. When frozen, TDI is an opaque white solid. It usually forms on the tank car walls, bottom valve areas and on the two-inch eduction tubes. Since it is often difficult to see frozen TDI in these locations the contents may be frozen, though no white solids are visible to the inspector. It is for this reason Olin recommends the car temperature be measured, by the methods described above.

When to Heat a TDI Tank Car

If the TDI temperature is less than 17°C (62°F), or if frozen TDI is detected visually, the car should be heated before it is unloaded.

[a]Fisher Scientific, Catalog #15-09.

Figure 10. Steam/Water Mixing System



If the car is not to be immediately heated or unloaded, it should be repressurized to 25 psig with nitrogen or dry air (−40°C dew point). Otherwise polyurea may form as the result of contamination of the TDI with water.

Heating a TDI Tank Car

The TDI should be heated to 32°C (90°F) until all the frozen TDI has thawed. Never allow the TDI temperature to exceed 43°C (110°F). If TDI is overheated dimerization takes place (see page 2). If this occurs the product should not be used.

Heat sources. The best way to thaw frozen TDI is with tempered hot water, thermostatically controlled to 41°C (105°F). Hot water is less likely than steam to cause dimerization.

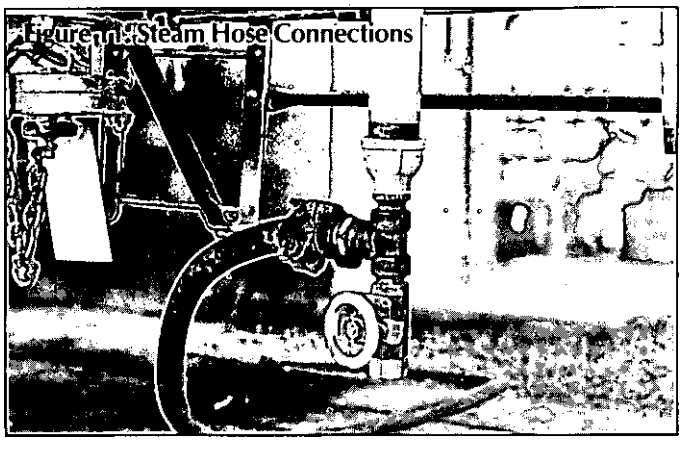
If tempered hot water is not available, an alternate source of heat is 20-lb steam, mixed with cold water. A steam/water mixing system similar to the one shown in Fig. 10 can be used to obtain the desired temperature.

Plants that have only steam available should avoid pressures above 20 lbs. High pressure steam, if not watched very carefully, will rapidly overheat the TDI. Even at lower pressures, careful monitoring must take place.

Heat source connections. Olin has a mixed fleet of tank cars that were designed by different tank car manufacturers and put into service at different times. Therefore, cars must be carefully examined to determine the size and location of the external coil inlets and outlets.

In general, the inlet is on one side of the car away from the handbrake (Fig. 11). If there are two inlet valves, the one farthest away from the handbrake side is for the left side coils; the one nearest the handbrake side is for the right coils.

Cars with a bottom outlet valve may have a separate inlet and outlet coil around this valve. If they must be used, they should be hooked up separately. When thawing bottom valves, take care not to damage the valve seats or to form dimer in and around the ball. This could prevent the valves from opening.



After the TDI is Thawed

After the TDI has been heated to 27°C, the entire contents of the car must be mixed to eliminate isomer ratio separation. There are two ways to mix the car's contents thoroughly.

First is to have the railroad move the car around for about two hours. Second is to unload the entire contents into a bulk storage tank. The TDI should then be recirculated for two to three hours.

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STORAGE OF TDI

Toluene diisocyanate may be stored indoors or outdoors. If TDI is stored indoors, the building should have sprinklers, good ventilation and adequate heat to maintain storage temperature of 21°C (70°F). Constant monitoring of TDI temperature is required.

If TDI is stored outdoors, or if indoor temperatures may drop below 21°C, provisions must be made for warming and thawing the TDI. These include adequate tank and line insulation, external heating coils or jackets, and steam-traced or electrically heated lines.

If thawing is necessary, never heat the TDI above 43°C (110°F). Overheating will cause dimer formation (see page 2). After thawing, mix the TDI to eliminate isomer separation. Use a tank agitator or a pump (recycle from top to bottom).

Whether indoors or outdoors, bulk storage tanks should be blanketed with nitrogen. Without this dry atmosphere, water vapor will react with the TDI to form solid polyurea which can plug lines and foam machine heads.

A pneumatic bubbler gauge[a] that operates with nitrogen is recommended. This gauge measures the pressure required to displace TDI from a vertical tube in the tank.

Storage Tank Design

Vertical, cylindrical steel tanks are normally preferred for storing TDI, although limited indoor headroom may dictate the use of horizontal tanks.

Vertical tanks use minimum ground space. This means less surface area is exposed to cold weather, and problems relating to heating and insulating are minimized. Vertical cylindrical tanks have a uniform cross section, and are gauged more readily than are horizontal tanks.

Storage tanks may be field-erected on a concrete foundation and there is no practical limitation to size. Recommended capacity is 30,000 gallons for tank car deliveries and 6-8,000 gallons for tank trucks. In other words, capacity should be sufficient to accept the entire contents of a tank car or truck even when half-filled.

Materials of Construction

TDI tanks can be made from carbon steel (ASTM A 285 Grade C) or from stainless steel (Type 304 or 316). API Code 650 specifies ¼" steel for the bottom; 3/16" for the shell and roof. Stainless steel tanks require no lining. Carbon steel tanks should have a baked phenolic lining. Recommended are: Heresite P 403[b], Lithcote LC 73[c], or Amercote 75[d]. The inside surface should be sandblasted to a commercial finish and cleaned prior to the application of the lining.

Hose and Piping to Receive TDI

From tank trucks. TDI is discharged by a built-in pump on the truck through flexible hose provided by the trucker into piping supplied by the customer. The length of the hose is specified by the customer with his first order. The piping should be Schedule 40 steel, or Aluminum Alloy 3003.

From tank cars. TDI is discharged through flexible hose into piping to the storage tank. Both the hose and the piping are provided by the customer. The hose should be lined with butyl rubber or non-virgin TFE (for piping materials, see above).

For bottom unloading of TDI, a positive displacement or centrifugal pump of adequate capacity is required. The pump should be made of alloy 20 or stainless steel with welded parts. Mechanical seals should be of the same materials, with O-rings of butyl rubber or non-virgin TFE.

When top unloading, it is also necessary to pressurize the car. Pressure should be 10-20 psig nitrogen or dry air, through a ¾-in reinforced rubber hose attached to the 1-in gas inlet quick disconnect. An oil and water separator and pressure regulator are also suggested as an assembly in the line near the fitting for the quick disconnect attachment.

Auxiliary Equipment

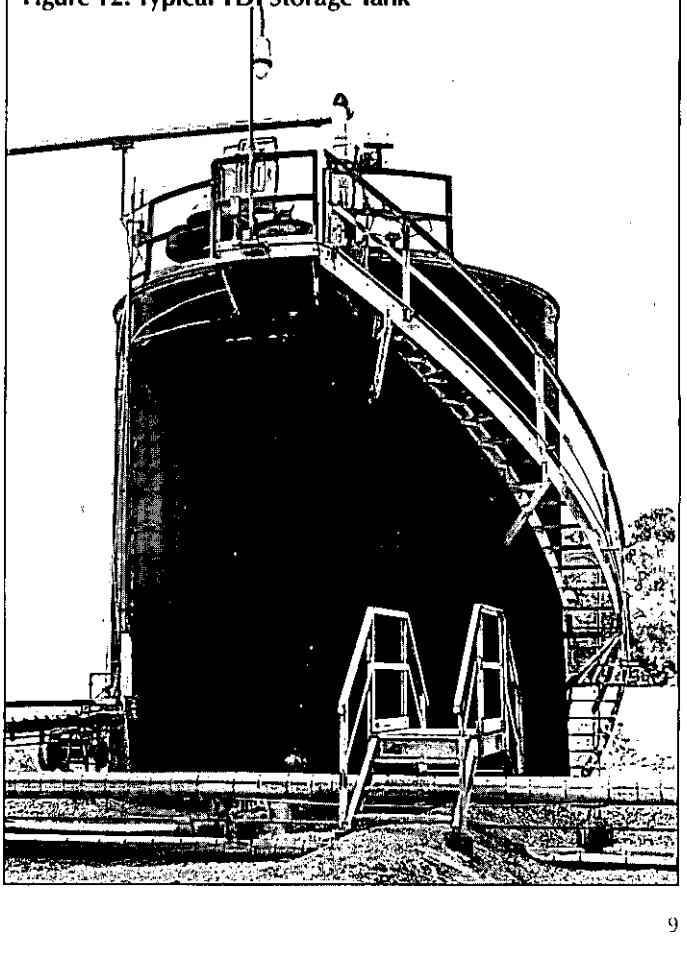
Valves. Ball valves should be stainless steel with non-virgin TFE seals. Plug valves should be stainless steel or alloy 30, with non-virgin TFE sleeve. Valves may be threaded or they may be flanged (150-lb ASA or MSS).

Filter and pressure gauges. A filter should be placed in the piping between the tank car or tank truck and the storage tank. A cartridge filter with 20- or 30-micron glass fiber element is recommended.

Pressure gauges should be installed on either side of the filter to measure the drop. This will indicate when the filter must be cleaned or replaced.

Sampling valves. If delivery is by tank car an in-line sampling valve is recommended (see page 4).

Figure 12. Typical TDI Storage Tank



[a]Petrometer Corp., New Hyde Park, NY, or Varec Div., Emerson Electric Co., Garden Grove, CA
[b]Heresite and Chemical Company, Manitowoc, WI
[c]Lithcote Corporation, Cherry Hill, NJ
[d]Amercon Corporation, Altoona, PA

HANDLING TDI

Toluene diisocyanate is a toxic and highly reactive compound. It should be kept in closed, isolated systems and transferred with care. However, TDI is not a difficult material to handle. If proper procedures are followed there is relatively little chance of danger.

The following sections briefly discuss some possible hazards and describe what to do in an emergency. Plant personnel should be thoroughly familiar with these procedures.

Reactivity Hazards

TDI is a stable compound with a relatively high flash point. However, it will react with water, acids, bases, and other organic and inorganic chemicals. TDI is also affected by heat and, like any organic compound, will burn.

Water. When TDI comes in contact with water, aromatic poly-substituted ureas are formed, heat is generated and carbon dioxide is evolved. Pressure build-up from the carbon dioxide will occur. This pressure could rupture a storage vessel.

To help prevent reaction with water the TDI should be kept under a nitrogen or dry air (−40°C dew point) pad.

Chemicals. TDI is a base and contact with acids should be avoided. Contact with bases, such as caustic soda, tertiary amines, etc., might cause uncontrollable polymerization. The heat given off could then rapidly vaporize solvent that might be present, again causing pressure build-up and risk of rupture of the storage vessel. High temperatures may also cause dimerization.

TDI should be kept away from rubber and plastics. These materials will rapidly become embrittled, cracks may develop and their strength may be weakened.

Fire Hazards

The flash point of TDI is 132°C (270°F) and therefore does not constitute a severe fire hazard. However, it should be remembered that TDI is an organic material and will burn when exposed to fire. In addition, the flash point of TDI does not reflect the hazards presented by any cellular or foam plastic product which contains TDI.

Health Hazards

TDI can be dangerous to health in either its vapor or liquid forms. Exposure to TDI vapor should not exceed 0.02 ppm at any time. However, it is difficult to detect TDI by its odor until it has reached 0.4 ppm. In other words, if TDI can be smelled, there is already too much vapor present. Therefore an OSHA- or NIOSH-approved TDI monitor should be used.

Some people develop an acute sensitivity, even at very low concentration. For this reason, pre-employment physical examinations should exclude persons with chronically recurring pulmonary disease or allergic history.

Inhalation. TDI is toxic from inhalation exposure. If inhaled, it may cause difficulty in breathing and irritation or injury to the lungs. Inhalation may also produce allergic sensitization to the respiratory tract.

Safeguards against inhalation include adequate ventilation, detection devices and respirators. The respirator (self-contained or air-line type) should only be worn temporarily while adequate ventilation is being reestablished.

Dermal and oral exposure. Toxicity from dermal or oral exposure is low. The acute oral LD_{50} (rats) is approximately 5.7 g/kg. However, TDI is irritating to the skin, eyes and mucous membranes, and may cause burns if not removed rapidly. Protective clothing, including goggles, should be worn whenever there is a likelihood of contact with TDI (see Figure 13).

Ingestion of TDI can cause severe irritation of the gastrointestinal tract. TDI should be stored away from foodstuffs. And food should not be eaten where TDI might be present.

Protective Clothing

Because of the health hazards associated with TDI, full protective clothing and equipment should be worn wherever there is a possibility of contact. Such occasions include (but are not limited to):

- When opening tank car hatches, truck manway covers or drum plugs
- When connecting and disconnecting hoses and pipes
- When placing and operating pumps
- When breaking TDI piping, even if previously decontaminated
- When flushing out drums

At other times, outer clothing made of cotton or a suitable synthetic fiber — plus a rubber apron for extra protection — should be worn.

If any article of clothing should be contaminated, remove it immediately and discard properly (contact with TDI damages both natural and synthetic fibers).

What To Do In Case Of . . .

White precipitates. There are three causes of white precipitates in TDI: dimer (caused by excessive heat), polyurea (caused by the presence of water), or frozen TDI. If it is not obvious which of the three is present, then heat the crystals. If they melt at 16-21°C (60-70°F) they are frozen TDI. If they melt at 150-160°C (302-320°F) then they are dimer. If they do not melt they are polyurea.

If the crystals are frozen TDI then the TDI can be thawed, remixed and used. If the crystals are polyurea then they can be filtered out and the remainder of the TDI can be used. However if the crystals are dimer then they cannot be completely removed (dimer reforms on filtration). The TDI should not be used because the dimer will affect physical properties as well as clog lines and foam heads. If dimer is present, contact Olin.

Discoloration. Normal TDI is water-white to light straw in color. If the color is darker than this the TDI has been exposed to light or high temperature. If the color is something other than water-white or yellow then the TDI has been contaminated and should not be used; call Olin for assistance.

If the TDI color has darkened, assume it has been caused by high temperature (the chances of light-induced discoloration are negligible). Since high temperature may also cause dimer formation the TDI should be tested. Simply cool a sample to room temperature. If white crystals precipitate, then dimer is present and the TDI should not be used. If there are no white crystals present then the TDI may be used. The discoloration will not affect physical properties or foam color.

Figure 13. Protective Clothing and Equipment

Hard Hat
(other than aluminum). Should have wide brim to protect against falling objects and overhead leaks and splashes.

Chemical Safety Goggles.
Required for all persons handling TDI.

Protective Suit.

Plastic Face Shield.
Worn if there is possibility of TDI splashing near the face.

Respirator.
Should be self-contained or air-line type. Should be worn only as a temporary measure until adequate ventilation is reestablished.

Protective Gloves.
Should be made of butyl rubber or disposable polyvinyl chloride (PVC).

Trouser Bottoms.
Should extend over boot tops.

Protective Boots.
Should have safety toes. Rubber overshoes may be worn with ordinary work boots. Do not wear uncovered leather shoes.

EMERGENCY ACTIONS

The following section contains basic information on what to do in the event of an accident. If additional information is necessary, call the Olin Product Emergency Service (OPES). Speedy advice from experts can be received 24 hours a day by calling:

(203) 356-2345

You will be asked to give a brief description of the emergency and leave your name and phone number. Shortly after, you will receive a return call from someone experienced with TDI who will advise you of immediate action to be taken.

In addition, the Chemical Manufacturers Association has established CHEMTREC to give advice on spill, leak or fire emergencies involving transportation and transport equipment. The CHEMTREC number is:

(800) 424-9300

In the District of Columbia, call 438-7616. If calling from Canada, dial (202) 483-7616.

First Aid

If there is known contact with toluene diisocyanate, take the following steps:

Eye or skin contact: Flush thoroughly with water. Call a physician.

Inhalation. Remove victim to fresh air. Call a physician.

Ingestion: Wash out mouth with water. Give plenty of water to drink, but do not induce vomiting. Call a physician.

Some symptoms of overexposure to TDI vapors include tightness in the chest, watering eyes, dry throat, and headaches. These symptoms may not appear until several hours after initial exposure. If there has been the possibility of exposure, and if these symptoms do appear, a physician should be called.

Handling Spills & Leaks

The National Institute of Occuptional Safety and Health (NIOSH) publishes *Criteria for a Recommended Standard . . . Occupational Exposure to Toluene Diisocyanate.* In it, the following procedures are suggested:

When TDI leaks, or spills occur, only properly protected personnel should remain in the area. Leaking containers should be removed to the outdoors or to an isolated, well-ventilated area, and the contents transferred to other suitable containers. [See "Leaking Drums", below.]

Adequate preparation and facilities for handling spills should be provided. These include suitable floor drainage and ready accessibility of hoses, mops, buckets, and absorbent materials. Spills should be cleaned up promptly.

The effectiveness of water is considerably improved by the addition of 1-5% ammonia. This solution is further improved by the addition of up to 10% isopropyl alcohol. [In cold weather, Olin recommends using a 50-50% mixture of isopropyl alcohol and perchloroethylene.]

Other absorbent materials such as sawdust or vermiculite are also useful in facilitating clean-up of spills. Such materials, after use, should be shovelled into an open-top steel container, the container then covered and removed to a safe disposal area away from the operating area.

The mixture should be soaked with water containing ammonia and allowed to stand for 24 hours in an open or partially open container.

Only after all the TDI has been neutralized should the container be sealed and disposed of according to appropriate Federal, state and local regulations.

Leaking Drums

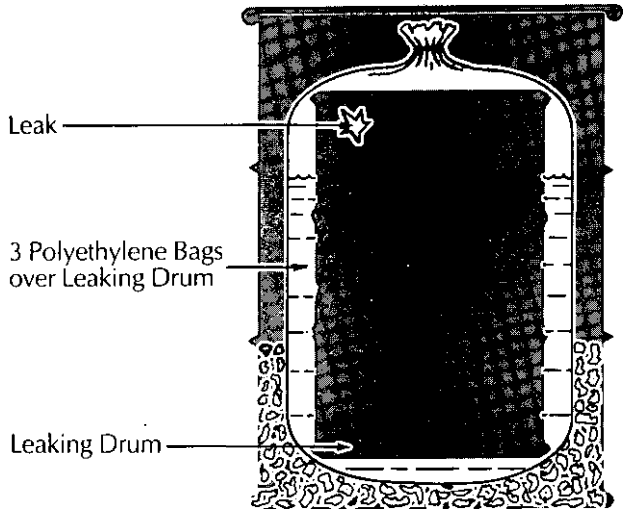
Invert the drum to stop the leak. The spilled TDI should be disposed of as described above. Then call Olin Technical Services:

(203) 789-6073 (8:30 AM-4:30 PM, Eastern Time)

(203) 356-2345 (all other times)

A 65-gallon salvage drum (Figure 14) will be sent to you. The original drum should be packed in a polyethylene bag within the overpack drum, marked "toluene diisocyanate UN2078," labeled "poison" and then returned to Olin.

Figure 14. Salvage Drum



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A word about Olin Corporation

Olin ranks high in Fortune Magazine's directory of leading U.S. industrial companies. It has sales of $2 billion, over 20,000 employees, 37 plants in 23 states and 16 manufacturing operations in 10 foreign countries.

But we're more than just numbers, and we'd like you to understand us better. You know of Olin Chemicals. And though you may not realize it, you've probably met our other five operating groups — Consumer, Brass, Ecusta Paper and Film, Winchester and Olin-American, through some of the things they make or do. For example:

Our Consumer Group makes Omalon® carpet foundation, Olin® skis, and signal flares, plus HTH® and Pace® swimming pool sanitizing chemicals. HTH is the largest-selling brand of pool water sanitizer in the world.

Our Brass Group produces brass, bronze and copper sheet and strip. It is the largest supplier of coin material to the U.S. Mint.

Our Ecusta Paper and Film Group is a major producer of cigarette papers, and one of only two U.S. suppliers of cellophane.

Our Winchester Group makes world-famous Winchester Western® sporting ammunition, as well as ammunition for national defense.

Olin-American is our real estate subsidiary, building homes and community developments across the nation.

In addition, Olin produces Ramset® powder-actuated tools, Weaver® scopes for sporting arms and proprietary seeds.

The Olin Chemicals Group

Taken alone, this Group could well be a major U.S. corporation. In 1981 Olin's sales of chemical products exceeded $1 billion.

Olin is a major producer of commodity inorganic chemicals. In fact, of the eleven chemicals most widely used in industry, Olin makes nine.

Olin also produces more specialized organic and inorganic chemicals. We're a leader in sodium phosphates, fluorides and chlorite used for treating industrial and municipal water supplies. Olin is the only U.S. manufacturer of synthetic sodium nitrate and sodium chlorite. We're the largest U.S. producer of ring-fluorinated aromatic derivatives.

We're the nation's largest marketer of hydrazine, the propellant that put our lander on the moon, and is helping to make the space shuttle a reality. On earth, hydrazine and its derivatives have important though less esoteric uses, like keeping industrial boilers from rusting, making soap more slippery, and protecting crops from weeds.

Olin is one of the largest marketers of ethylene and propylene glycol ethers in the U.S. They're used in such diverse products as solvents, paints, household cleaners, insecticides and functional fluids.

You'll find our products on the farm. Our ammonia and urea go into fertilizers that help raise crops. Our Terraclor® and Terrazole® fungicides protect them during growth.

You'll find our products in the home. Olin urethanes go into upholstered furniture and refrigerator insulation. Our blowing agents are used to make vinyl flooring. Your shampoo may contain our Omadine® antimicrobial agent, the active ingredient in most anti-dandruff shampoos throughout the world. Your household detergents may contain our sodium phosphates and Poly-Tergent® surfactants.

You'll find our products used in your clothes. Our Reductone® sodium hydrosulfite and Dyetone® sodium bromate are basic chemicals for textile dyeing. And we supply key intermediates for dyestuffs.

You'll find our products in your car. Olin is one of three primary manufacturers of brake fluid in the U.S. And Olin urethane chemicals are used to make everything from seat cushions to impact-resistant bumper systems.

In fact, wherever you live, however you travel, whatever you do, chances are your life is touched in some way by the chemical products made by Olin.

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